Atomic structure of metal-oxide interfaces. Studied by high resolution electron microscopy

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SUMMARY

This thesis deals with the atomic structure of interfaces between metals and oxides. A principal feature of the atomic structure of these interfaces is the fact that the lattice parameters of the two constituents usually do not match, leading to a certain geometrical misfit. Consequently atoms near the interface do not all have the same local environment. If there is an physical interaction across the interface this will result in energy differences between the atoms, some of them residing in more comfortable position than others. The energy of the interface can be lowered if some of the atoms move towards these favourable positions while others are forced into unfavourable positions. This results in the formation of regions where coherence has increased, and other areas where coherence has decreased. The latter are interpreted as the cores of misfit dislocations.

The degree and nature of these relaxations near the interface depend on the geometry of the interface and on the bonding across it. Hence, by imaging the atomic structure it is possible to study the bonding at the interface.

In this thesis the atomic structure of metal-oxide interfaces is *measured* as well as *calculated*. The experimental procedures and techniques are introduced in chapters 2 and 4, the experimental results in chapters 5 and 6. Chapter 3 describes the methods used for the calculations.

To experimentally determine the atomic structure we used High Resolution Transmission Electron Microscopy (HRTEM). The interfaces were created in two different ways: internal oxidation and Molecular Beam Epitaxy. Both methods lead to the formation of atomically flat interfaces that can be studied with HRTEM. Most of the results discussed were obtained on interfaces created with internal oxidation.

An atomistic description of the interface was used that, although simple, describes essential features of the interaction across metal-oxide interfaces. The interaction between atoms in the metal is described with a many-body interaction function, and the interaction across the interface with a pair-wise interaction function. The oxide is assumed to be rigid. The power of the description lies in the possibility to vary misfit

as well as the strength of the interaction across the interface. Using this model we investigated how interface energy and structure depend on misfit and bond strength, for a relatively simple interface. This is described in chapter 3. It appears that the localisation of the cores of the misfit dislocations increases with increasing bond strength, and also that for constant bond strength the localisation is stronger for low values of misfit. It is concluded that, in principle, the core structure of misfit dislocations may provide information on the bond strength and the interface energy. The results of these calculations are compared with an approach based on anisotropic linear elasticity theory. In general we learned that a fair correlation exists between the atomistic and elastic continuum description of interface dislocations. However, it is shown that the elastic continuum approach cannot account for the possible configurations at an interface with misfit, because it does not enlighten the effects of different bond strengths on the interface structure.

In chapter 5 we discuss the structure of a number of interfaces of the cubic oxide MgO with fcc metals. Emphasis is on the structure of the {111} interface between Cu and MgO. For this interface we find a reasonable correspondence between the experimental and the calculated structure. The structure differs from other proposed structures for the same interface. The striking difference is that the structure is characterised by the presence of misfit partial dislocations rather than undissociated VOLTERRA dislocations. The energy difference between a number of different configurations with different symmetry at the interface appears to be a crucial factor in determining this structure. This appears to be an important observation, of more general validity for metal-oxide interfaces.

In chapter 6 interfaces between Ag and the hexagonal oxide ZnO are discussed, created with internal oxidation. In this system we found several different interfaces at which a vicinal or stepped Ag plane is in contact with a low index ZnO plane. On these interfaces similar and rather complicated relaxations were found to be present. Based on the geometry of the interface, and on the experimental evidence, a physical picture of the relaxations is proposed. In this picture, the array of steps at the metal side, that closely resembles an array of $1/3\langle 111\rangle$ FRANK partial dislocations, dissociates in $1/6\langle 121\rangle$ SHOCKLEY partial dislocations a short distance away from the interface, and $1/6\langle 110\rangle$ partial stair-rod dislocations at the interface. The validity of this picture was tested using the atomistic as well as the anisotropic linear elasticity approach, both of which confirmed that it correctly describes the relaxations at the interface. Interestingly, the distance between SHOCKLEY and "stair-rod" appears to

depend on the distance between the original steps at the interface in the calculations as well as the experiment. These observations are important, because they show that it is possible vary the dislocation density, or in other words the misfit, at interfaces in certain metal-oxide systems. This means that meanwhile the interaction at the interface remains the same. Because it appears to lead to measurable differences in structure this may prove to be an excellent way to study the interplay between misfit and bond strength in an experiment.